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I also certify that the attached copy of the request for grant of a Patent (Form 1/77) bears an amendment, effected by this office, following a request by the applicant and agreed to by the Comptroller-General.

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Signed Andrew Gersey

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1. Your reference — BC9/Z

2. Patent application number *(The Patent Office will fill in this part)* — **9817094.7**

3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

THE UNIVERSITY OF WALES. BANGOR
BIOCOMPOSITES CENTRE
BANGOR
GWYNEDD
LL57 2UW

Patents ADP number *(if you know it)* — 7269319002.

If the applicant is a corporate body, give the country/state of its incorporation

4. Title of the invention

IMPROVEMENTS IN OR RELATING TO THE UTILIZATION OF RESOLE RESINS

5. Name of your agent *(if you have one)* — ~~NONE~~

"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

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Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*

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Number of earlier application	Date of filing *(day / month / year)*

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   a) any applicant named in part 3 is not an inventor, or
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Description	14
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Priority documents	
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Statement of inventorship and right to grant of a patent *(Patents Form 7/77)*	1
Request for preliminary examination and search *(Patents Form 9/77)*	
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11. I/We request the grant of a patent on the basis of this application.

Signature JAMES BOLTON (DIRECTOR) Date 4.8.98

12. Name and daytime telephone number of person to contact in the United Kingdom SARA HUGHES 01248 370588

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Improvements in or relating to the utilisation of resole resins

This invention relates to improvements in the utilisation of resole resins in the manufacture of bonded products from lignocellulosic materials such as plywood and phenolic resin bonded particle board, in which an additive, maleic anhydride, which may be converted to maleic acid, is used during manufacture to achieve significant benefits over existing manufacturing processes.

We have found that maleic anhydride can be used to either to achieve cost savings by reducing the quantity of resin required to achieve a lignocellulosic product with adequate performance, or to enhance the performance that can be achieved with a particular quantity of resin and particular manufacturing conditions.

The pre-treatment of wood particles with dibasic anhydrides to produce an esterified woody material is described in GB 2,136,004, and the esterified material is used to form a moulding, by mixing it with an epoxy resin. The esterification reaction is carried out in the presence of a catalyst and, as exemplified, the reaction times used vary from 7.5 minutes to 15 hours, the longest reaction times being used where the wood particles are chips of the kind used for producing particle boards. The product made in GB 2,136,004 is not a particle board but a moulded wood product with a smooth and lustrous plastic like appearance. The specification includes a comparative example in which a

particle board is made using a phenolic resin, but there is no suggestion to use the esterified wood in the manufacture of particle boards.

USP 5,520,777 discloses a method of making fibreboard which includes forming a condensate of maleic anhydride and glycerol and impregnating wood chips with this condensate before the chips are transferred to a digester where, during steaming at an elevated pressure, an esterification reaction takes place between the components of the wood and the condensate. After digestion, the treated material is refined i.e converted to fibre form under pressure. We have found that it is not

necessary to go to the expense of converting the maleic anhydride into a condensate when treating particle board. We also avoid the need to impregnate the wood component, merely applying the maleic anhydride either to the wood surface or admixing it with the phenolic resin. The extreme conditions required to esterify the lignocellulose component of the wood and any chemical reactions which may occur during the refining process clearly distinguishes the manufacturing process of USP 5,520,777 from the proposals of the present invention.

USP 4,961,795 acknowledges at column one lines 35 to 45 that acids have been added to resole resins to accelerate the cure of PF resins, and the prior art cited against this specification includes several specifications in which acids are added to PF resins, either to control the rate of curing, or to increase the shelf life of resole resins whose initial formation involved manufacture at relatively high alkaline pH, as the higher the pH the shorter the shelf life of the resin. This means that if resins are e.g manufactured at ph 11, the pH will be reduced to say 7 by the addition of e.g sulphuric or oxalic acid before the resin is sold for use. USP 4,011,186 describes such a process for stabilising a resin. USP 4,961,795 describes the use of curing agents for phenol-formaldehyde which have an ester functional group selected from the group consisting of lactones, organic carbonates, carboxylic acid esters or mixtures thereof. These curing agents are added to the resin prior to its addition as a binder, and in order to to avoid unacceptable increases in the viscosity of the resin so reducing the pot life of the resin as it becomes too viscous to handle a further additive in the form of an aliphatic alcohol is added to moderate the effect of the curing agent. There is no teaching in the specification concerning the pH at which curing takes place, but where it is possible to deduce this from the examples, it appears curing takes place at alkaline or neutral conditions.

The manufacture of particle boards involves the steps of forming a mixture of wood particles, phenolic resin, and other additives and forming the mixture into what is known as a mattress. This mattress is then pressed into its final board shape while heat is supplied to cure the resin. The time required to cure the resin so as to achieve satisfactory products is one of the factors determining the cost of the finished product as it governs the throughput that can be achieved. One form of our

invention relates to the manufacture of such boards where the resins used are resole resins, i.e resins at a stage where formaldehyde and phenol have already been reacted in the presence of alkali to form oligomers which then readily polymerise when heated during pressing to bond the finished board. A satisfactory cure is needed to ensure that the final properties of the board are adequate for any particular end use. Such properties include water resistance, which is measured by examining the swelling of finished boards after soaking in water, and internal bond strength. We have found that maleic anhydride and maleic acid when added to the wood particle mixture prior to pressing can assist in obtaining a larger throughput of boards, because of a faster cure, and also gives an improvement in internal bond strength and water resistance over boards made under comparable conditions in the absence of the additive. An added advantage of the use of such additives is that the boards are a much lighter colour than those obtained simply using a resole resin.

Maleic anhydride is an acidic material and in the presence of water undergoes conversion to maleic acid and on heating maleic acid decomposes into maleic anhydride and water. Maleic anhydride will therefore form maleic acid when added to a wood particle mixture in water or in the presence of water, and it is possible that some or all of the maleic acid may take part in the curing process through conversion to the anhydride. This also applies to the direct addition of maleic acid in a solid form.

Maleic anhydride's ability to become incorporated into the resin matrix is probably due to the electrophilic nature of the maleic anhydride molecule under the conditions used in forming a phenolic resin. We have found that other acidic anhydrides such as phthalic and succinic anhydride do not produce the same benefit, possibly because they do not possess a suitable combination of acidic and electrophilic properties when curing a resole resin under acid conditions. Strong acids, such as sulphuric acid, while capable of producing an improved product in terms of bond strength and water resistance, cannot be used because of the possibility of causing corrosion of the manufacturing plant, and in addition cause discolouration of the resin which can be seen in the finished product, which is unacceptable from a marketing point of view. Maleic acid and

anhydride, though weaker acids, unexpectedly give a product equivalent in performance without the disadvantages arising from the use of strong acids.

According to the invention, therefore, there is provided a method for improving the utilisation of resole resins as bonding agents in the formation of products from lignocellulosic materials, in which at least one of maleic anhydride and maleic acid is added during the formation of such products so as to be in admixture with the resin when it is cured to bond the product..

There are several forms of bonded lignocellulosic products which utilise resole resins as a bonding agent, such as plywood and various forms of particle board. Wood can be used in particle board in the form of fibre, chips, shavings, and flakes. Our invention is particularly applicable to the manufacture of particle board and will be described and exemplified by reference to the manufacture of such products.

Our invention therefore also includes in a process for manufacturing phenolic resin bonded wood particle board in which a mixture of wood particles and a resole phenolic resin are formed into a cured board under the action of heat and pressure, the improvement of providing in the mixture prior to pressing to form the cured board, at least one of maleic anhydride and maleic acid.

Particleboard is formed by placing a particulate form of wood such as wood shred in admixture with a phenolic resin mixture in a press, and then pressing it with a heated platen to e.g 12 mm stops at an elevated temperature e.g 200^{o} C. for several minutes. It is necessary to ensure that at its core the material being pressed reaches a high enough temperature for a sufficient time to cure the resin. The final dimensions of the product depends on the shape of the press and the pressure applied by the platen.

Water can cause products made in this way to deteriorate. A loss of bond strength with consequential swelling of the board, and in severe cases disintegration of the board, can occur. It is

desireable to improve the ability of such product to resist attack by water so as to obtain a product with high dimensional stability.

We have now found that the addition of maleic anhydride or maleic acid not only increases the dimensional stability of the boards, compared to boards made without the addition of maleic anhydride, but the cost of the product is also reduced. Maleic anhydride/acid costs less than the phenolic resin for which it may in part be substituted.

Our invention also includes dissolving maleic anhydride in water, thus forming a maleic acid solution and adding the maleic anhydride in this way to the system. It is possible that some or all of the maleic acid may react in the system in the anhydride form through decomposing back to the anhydride during the application of heat and pressure.

Maleic anhydride is added to the wood particle mix prior to the formation of the board. As a solid, it may be added at the same time as the resin to the wood particles, or incorporated into the wood particle mix prior to adding the resin. In forming phenolic resin wood particle boards, it is common to incorporate a wax emulsion into the mix. Maleic acid may be incorporated into the wax emulsion prior to its addition to the wood particle mix as a solid or a solution.

The quantity of maleic anhydride or maleic acid added is in the range 5-55% by weight of resin and preferably 15-40% by weight of resin.

The combined amount of resin and maleic anhydride or acid used will vary according to the requirements of the product but usually ranges from 2% to 15% by weight of dry wood. Measurements are based on dry wood content but the wood chips used can contain as much as 14% by weight of water, and do not necessarily need to be dried before use.

Our invention does not exclude the use of mixtures of maleic anhydride and maleic acid though there is no advantage in doing so as it simply means that two raw materials have to be utilised rather than choosing one.

A suitable wax emulsion of a microcrystalline wax is that sold under the trade name Mobilcer 538 by Mobil Ltd. We have found that a mixture of maleic acid and wax emulsion is made more stable by the further addition of a polybutene emulsion such as that sold by BP Chemicals under the trade name Hyvis polybutene.

Wax is sometimes added in the manufacture of particle board in a molten form, and in this case is usually sprayed onto the wood particles. In such a case, molten maleic anhydride may be sprayed onto the wood particles before spraying with molten wax. Molten maleic acid may also be used in the absence of wax. It can conveniently be sprayed onto e.g wood chips during the final stage of a drying process and the particles then sprayed with a resole resin in water.

A well known commercial form of particle board is oriented strand board (OSB). OSB is made from wood strands produced by slicing and milling wood. The strands will typically have dimensions of the order of 50mm x 10mm x 2 mm. The strands after drying are sprayed with hot wax and mixed with powdered phenolic resin. The strands are then formed into a mattress which is pressed for at 200° C. to cure the resin. The pressing time is measured in so many seconds per mm thickness of the mattress, and is typically chosen from the range 20-40 seconds per mm. The present invention could be applied to such a commercial process by adding maleic acid solution to the wood in the dryer, or spraying molten maleic anhydride along with the hot wax,. The molten wax can also be replaced by a wax emulsion to which a solution of maleic acid has been added.

The following examples illustrate but do not limit the invention.

In all of the examples the PF resole resin used is a commercially available resole resin sold by Neste Chemicals Ltd under the designation BD937. The boards were pressed at 200°C in a 150mm die to 12mm stops with a pre-heated punch. The test samples were conditioned according to the method of BS5669 before being tested for internal bond strength, thickness swell after 24 hours soaking in water at 20°C, and retained internal bond after drying at 60°C and re-conditioning according to the method of BS5669.

Example I

A series of boards was made using softwood chips with a moisture content of 4%, resin powder, various acids, and a mixture consisting of 80% by weight of Mobilcer 538 and 20% polybutene emulsion. The quantity of wax mixture was 1.6% of the dry weight of wood. The various acids were mixed with the wax mixture before the wax/acid mixture was added to the wood. The quantity of maleic acid was used in the proportion of one part acid to three parts resin, dry weights. The other acids were added in sufficient quantity to maintain an equivalent molar ratio of acid to resin to that achieved by the maleic acid example. The acids used, and their effect on the colour of the cured resin, were:

Acidic material	pKa	resin colour
sulphuric acid	-9	Black
p-toluene sulphonic acid	-6.5	Black
trichloroacteic acid	0.7	dark red
dichloroacetic acid	1.48	light yellow
maleic acid	1.83	light yellow

After mixing in the wax, sufficient resin was added to make the total of dry weight of acid and dry weight of resin up to 5% of the dry weight of wood. The boards were pressed for three minutes. The internal bonds and thickness swells are shown in Graph I .

Example II

A series of boards were made to demonstrate the improved properties obtained by the addition of maleic acid. The wood was a softwood shred with a moisture content of about 6 per cent. The

wood shred was wetted with 2% by weight (based on the dry weight of wood) of Mobilcer 538, then 5% by weight of resin (again, dry wood basis) was stirred in.

Boards were made with either no maleic acid or with 25% or 40% of the resin replaced by maleic acid. The maleic acid was added to the dried wood shred as a 30% aqueous solution (calculated as weight of anhydride to weight of solution) made by dissolving maleic anhydride in water. The acid solution was added before the wax dispersion. The boards were pressed for 2½, 3, 3½, 4, 4½ and 5 minutes.

Graph II shows the internal bond strength (IBS) obtained after pressing for the times and temperature specified. Graph III shows the IBS after soaking the series of boards in water for 24 hours at 20°C. Graph IV shows the degree of thickness swell after the same treatment.

The results of these experiments clearly show the benefit of the addition of maleic acid in achieving the development of satisfactory IBS, both initially and after soaking, as well as swell resistance. One way of expressing the improvements achieved is in terms of the acceleration in the curing time i.e the reduction in time required to achieve a particular strength, both initially and after soaking, or in the time to achieve a low level of thickness swell. It can be seen that with the addition of maleic acid both initial IBS development and IBS after cold soak is accelerated by about 6sec/mm and swell resistance by about 5 sec/mm.

Example III

Either powdered maleic anhydride or powdered maleic acid was mixed with powdered BD937 resin in the ratio of one part to three parts. 3g of Mobilcer 538 wax emulsion was stirred into 265g of wood chips with a moisture content of 10% for one minute. 12 g of the mixture of resin and maleic anhydride was stirred in for a further minute. Control boards using 12g BD937 were made according to the same method. The boards were pressed for 3 minutes, 3½ minutes or 4 minutes. The boards made with maleic anhydride or maleic acid cured more quickly, had higher internal

bond strength, swelled less in cold water, and had higher retained internal bond strength after soaking, as shown in Graph V

Example IV

BD937 resin was made into a 50%, by weight, aqueous solution. 7.5% of the BD937 resin solution was mixed with wood chips, with a moisture content of 8.7%, for one minute and then 1.25%, by weight of dry wood, of maleic anhydride was mixed in for a further 1 minute. Control boards were made by mixing 10% of the BD937 resin solution, by weight of dry wood, with the wood chips. Boards were pressed for 3, 3½, 4, or 5 minutes. The boards made with maleic anhydride had higher internal bond strength, swelled less in cold water and had higher retained internal bond strength after soaking, as shown in Graph VI.

Examples V to XIII are provided to illustrate the various ways in which maleic acid and maleic anhydride may be added to improve the performance of resole resins. All the boards made when tested gave results of the same order as those obtained in Example I to IV.

Example V

Maleic anhydride was stirred into water to make a 30% w/w solution of maleic acid. Mobilcer 538 wax emulsion was mixed with Hyvis polybutene emulsion in the ratio 3:1. The maleic acid solution was mixed with the wax mixture in the ratio 10:3. 13g of this mixture was stirred into 250g of wood chips with a moisture content of 5.4% for 1 minute, followed by 9g powdered BD937 resin which was stirred in for 3 minutes.

Example VI

Maleic anhydride was stirred into water to make a 30% w/w solution of maleic acid. 10g of this mixture and 3g of Mobilcer 538 wax emulsion were stirred into 250g of wood chips with a moisture content of 5.4% for 1 minute, followed by 9g powdered BD937 resin which was stirred in for 3 minutes.

Example VII

Maleic anhydride was stirred into water to make a 30% w/w solution of maleic acid. 10g of this solution was sprayed onto 250g of wood chips with a moisture content of 11% while they were being stirred for 1 minute. 9g of powdered BD937 resin was stirred in for 1 minute.

Example VIII.

BD937 resin was made into a solution of 50% solids content. 18 g of this solution was stirred into 250 g of wood chips with a moisture content of 11% for one minute. 3 g of powdered maleic anhydride was then stirred in for 1 minute.

Example IX

BD937 resin was made into a solution of 50% solids content. 18 g of this solution and 3 g of powdered maleic anhydride were stirred into 250 g of wood chips with a moisture content of 11% for 2 minutes.

Example X.

BD937 resin was made into a solution of 50% solids content. 18 g of this solution was stirred into 250 g of wood chips with a moisture content of 11% for one minute. 3 g of powdered maleic acid was then stirred in for one minute.

Example XI.

BD937 resin was made into a solution of 50% solids content. 18 g of this solution and 3 g of powdered maleic acid were stirred into 250 g of wood chips with a moisture content of 11% for 2 minutes.

Example XII.

Molten maleic anhydride may be sprayed onto wood flakes as they emerge from a dryer at a temperature of around 50°C. The flakes are then sprayed with molten wax and powdered resin is added, as is common in the production of orientated strand board. The resinated flakes are laid up and pressed in the normal manner.

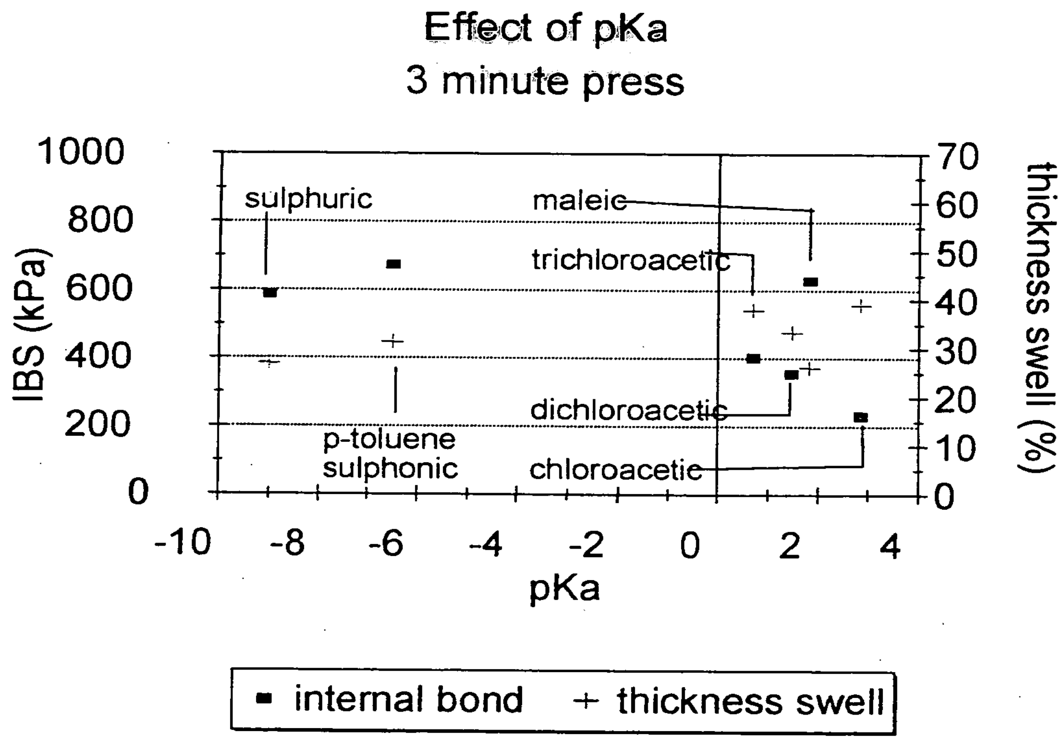
Example XIII.

Molten maleic anhydride may be sprayed onto wood chips during the final stage of drying. The chips are then sprayed with a solution of phenolic resin in water in the usual manner. No wax needs to be added as the mixture does not stick to the mixer or the conveyors. The resinated flakes are laid up and pressed in the normal manner.

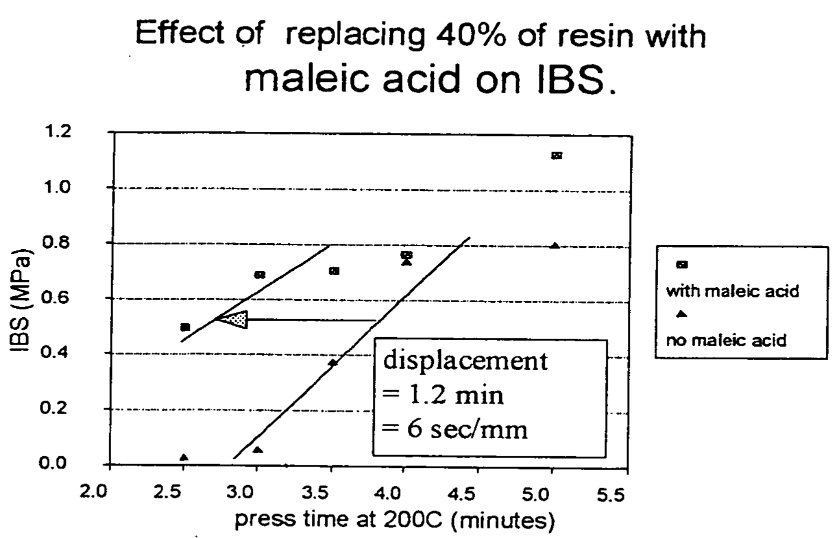
ABSTRACT

Improvements in or relating to the utilisation of resole resins

This invention relates to improvements in the utilisation of resole resins in the manufacture of bonded products from lignocellulosic materials such as plywood and phenolic resin bonded particle board, in which an additive, maleic anhydride, which may be converted to maleic acid, is used during manufacture to achieve significant benefits over existing manufacturing processes.



Graph I



Graph II

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